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A rare-earth Y-zeolite-containing catalyst for cracking hydrocarbons and a method for preparing the same

TECHNICAL FIELD

The present invention relates to a catalyst for cracking hydrocarbons and a method for preparing the same. More particularly, the present invention relates to a rare-earth Y-zeolite-containing catalyst for cracking hydrocarbons and a method for preparing the same.

TECHNICAL BACKGROUND

Recently, the requirement for the quality of hydrocarbon products has become more and more critical with the growing tendency for raw oil to become heavier and the increase of the consideration for environmental protection. In 1980's, the progress for preparing lead-free gasoline promoted the development of the catalytic cracking process and the catalysts. The Y-zeolite with high silica content as well as various catalysts and auxiliaries with high octane number were produced and used in the conversion of cheap heavy oil to the light products with high additional values.

The processing of inferior residuum has been long concerned with in petroleum refining industry. It is an important problem need to be resolved urgently that how to obtain fuel with high yield of light oil, less olefin and sulfur, as well as being environmentally friendly, when treating the inferior residuum and blending more residuum to the feedstock oil.

In USP3293192 and Society of Chemical Engineering (London) Monograph Molecular Sieves, P. 186 (1968), C. V. MC. Daniel and P. K. Maher reported a hydrothermal dealumination method used to prepare Y-zeolite with high silica content, since then the method has been widely used. US3,442,715 disclosed a dealuminated Y-zeolite (DAY), US3,449,070 disclosed an ultra-stable Y-zeolite (USY), US4,51,694 and US4,401,556 disclosed an ultra-stable hydrophobic Y-zeolite, *etc.* The ultra-stable Y-zeolite (USY) was widely used and developed because it has high Si/Al ratio, high hydrothermal stability, low hydrogen transfer activity and good selectivity of coke and can be used to

prepare catalyst with high octane number when treating heavy oil.

With the increasing development of heavy oil processing, the characters of ultra-stable Y-zeolite with high silica content, such as high Si/Al ratio, high hydrothermal stability and low hydrogen transfer activity, are no more suitable for the worse of the inferior heavy oil and cannot satisfy the environmental requirement on catalytic cracking cleaning fuel. It's urgent to find out a kind of zeolite, which has high hydrothermal stability, high cracking activity, good hydrogen transfer activity, stability and selectivity of coke, and the ability to decrease the olefin and sulfur content of gasoline effectively while increasing the conversion of heavy oil.

In order to increase the activity of Y-zeolite with high silica content, US4,840,724 discloses a method to increase the rare-earth content of ultra-stable Y-zeolite by rare-earth ion exchange. The process used to prepare Y-zeolite with high silica content (USY) through hydrothermal method has many hydrothermal exchange and high-temperature calcination procedures. In the process of dealumination with supplement of silica, a lot of dealuminated holes are formed and cannot be filled in time with the silica migrating from the skeleton, which usually leads to the collapse of the crystal lattice of the zeolite. The resulted silica and alumina fragments tend to block the channels of the zeolite and are not easily eliminated, which results in the low ion exchange level of the rare-earth. In the rare-earth ultra-stable Y-zeolite (REUSY), the highest RE_2O_3 content, used to express the rare-earth content, is only about 3% by weight after many times of ion exchange and calcinations. Such a low RE_2O_3 content is far from satisfy the requirement of high cracking activity and stable hydrogen transfer activity for the catalyst in the deep treating of inferior raw oil.

In order to increase the activity of Y-zeolite and utilize the high ion exchange capacity of NaY zeolite, REHY and REY zeolites with high rare-earth content through are prepared many times of rare-earth ion exchange and high-temperature calcination procedures to increase the rare-earth content of the zeolite. The RE_2O_3 content of REHY zeolite was increased to about 6~16% by weight and the RE_2O_3 content of REY zeolite was increased to about 8~20% by weight, which may satisfy the requirement of increasing the hydrogen transfer activity of the zeolite and thereby achieve the object of

increasing cracking activity.

But the use of hydrothermal method with many times of ion exchange between ammonium ion and rare-earth ion and high-temperature calcination usually leads to the collapse of the crystal lattice of REY and REHY zeolite. The resulted silica and alumina fragments tend to block the channels of the zeolite and are not easily eliminated, which in turn inhibit the effective migration of rare-earth ion (RE^{3+}) to β -cage of the zeolite. REHY and REY zeolites have a fatal defect in that the original crystal cell is hard to shrink, the Si/Al ratio is low, the unit cell size is of 2.470nm and the zeolite skeleton structure is not stable. As a result, the prepared catalyst shows high original cracking activity and hydrogen transfer activity, but is easy to be deactivated in reaction equipments, and the hydrothermal stability, the equilibrium activity as well as the equilibrium unit cell size of Y-zeolite used as active component are low. During manufacture process, a large amount of fresh catalyst need to be added to keep activity because of the rapid decrease of the activity, the lost of the original hydrogen transfer activity and the decrease of the coke selectivity of the catalyst. In the manufacture of hydrocarbons the low stability of cracking activity and hydrogen transfer activity of the catalyst results in a high consumption of the catalyst, a high product yield of coke and an unstable operation of the equipment. So they cannot be widely used in the deep treating of inferior raw oil and fulfil the purpose of manufacturing environmentally friendly fuel and decreasing the olefin content of gasoline.

DISCLOSURE OF THE INVENTION

The object of the invention is to supply a rare-earth Y-zeolite-containing catalyst for cracking hydrocarbons and a method for preparing the same in order to overcome the above shortcomings in prior art, said catalyst is suitable for treating inferior raw oil, manufacturing environmentally friendly fuel and decreasing the olefin content of gasoline.

The rare-earth Y-zeolite-containing catalyst for cracking hydrocarbons supplied by present invention is characterized in that the rare-earth content in crystal lattice of the rare-earth Y-zeolite, calculated in RE_2O_3 , is from 4 to 15% by weight, preferred from 6

to 12% by weight. The original unit cell size is from 2.440nm to 2.465nm, preferred from 2.445nm to 2.460nm, more preferred from 2.450nm to 2.458nm. The equilibrium unit cell size after 100% steam-aging treatment at 800°C for 17 hours is larger than 2.435nm, preferred than 2.440nm, more preferred than 2.445nm.

The content of the rare-earth Y-zeolite in the catalyst of present invention is from 10 to 50% by weight, preferred from 15 to 40% by weight, more preferred from 15 to 35% by weight.

The rare-earth Y-zeolite in the catalyst of present invention has a relatively high Si/Al ratio in the skeleton, and the Si/Al ratio is from 6 to 20, preferred from 8 to 15, more preferred from 8.3 to 8.8. The content of Na₂O is less than 1.0% by weight, preferred less than 0.5% by weight.

The rare-earth Y-zeolite in the catalyst of present invention has unblocked channels, in which the rare-earth ions (RE³⁺) can migrate from super-cage to β -cage effectively. Many more rare-earth ions (RE³⁺) enter β -cage of the zeolite and increase the stability of the crystal lattice. A large amount of rare-earth in β -cage could still be kept after strict steam-aging treatment and form stable hydroxyl structures. It is confirmed that the equilibrium unit cell size after 100% steam-aging at 800°C for 17 hours still keeps larger than 2.435nm, even larger than 2.440nm. Because of the difference of the original unit cell size, the zeolite has obvious structural stability with the equilibrium unit cell size changes from 2.435nm to 2.455nm. Due to the stability of the structure, the differential thermal collapse temperature of the zeolite is higher than 1000°C, preferred from 1000 to 1056°C.

The spectra of the hydroxyl structure characterized by FT-IR indicate that the typical peak 3540cm⁻¹ for hydroxyl structure of β -cage is clearly stronger than that of REY zeolite and REHY zeolite. The acidity spectra of B-acid characterized by FT-IR indicate that the acidity of B-acid and the stability of the acidity are far higher than those of REHY and REY zeolite. For instance, seen from Figure 1, the hydroxyl structural peak of β -cage near 3540cm⁻¹ for the rare-earth Y-zeolite (RHSY) with 10% by weight of RE₂O₃ used in the catalyst of present invention is obviously stronger than that of REY zeolite with 16.6% by weight of RE₂O₃, and much more stronger than that of REHY

zeolite with 13.6% by weight of RE_2O_3 . Seen from Figure 2, the acidity of B-acid for RHSY zeolite is far higher than that of REHY and REY zeolite.

The rare-earth Y-zeolite in the catalyst of present invention overcomes the shortcoming of REUSY zeolite with low rare-earth ion exchange degree and the shortcomings of REY and REHY zeolite with large original unit cell size, low differential thermal collapse temperature, and high Na_2O content as well as poor hydrothermal stability. The present rare-earth Y-zeolite not only has small original unit cell size, high Si/Al ratio and good hydrothermal stability just like REUSY zeolite, but also has high rare-earth content, excellent hydrogen transfer activity just like REY and REHY zeolite. At the same time it also overcomes the shortcoming of REY, REHY and REUSY with low equilibrium unit cell size and poor structural stability.

The catalyst disclosed in present invention may contain zeolite with MFI structure as cracking active component. The zeolite with MFI structure is selected from ZSM-5 or one or more of the zeolites with MFI structure, such as the five-ring rare-earth zeolite with high silica content (designated as ZRP) disclosed in CN1052290A, CN1058382A, CN1147420A and CN1194181A. This zeolite is prepared by using REY or REHY zeolite with rare-earth content of 2~23% by weight (calculated in oxide) and Na content less than 5.0% by weight as crystal seeds. The weight ratio of the zeolite with MFI structure and the rare-earth Y-zeolite is from 0.01 to 0.5.

The present invention also provides a method for preparing the rare-earth Y-zeolite-containing catalyst for cracking hydrocarbons, comprising the following steps:

- (1) The rare-earth Y-zeolite is dried till its water content less than 10% by weight, then in a weight ratio of SiCl_4 : Y-zeolite = 0.1~0.9: 1, reacts with SiCl_4 gas carried by dry air at 150~600°C for 10min to 6 hours, further is purged by dry air for 5min to 2 hours and washed by deionized water to remove the residual soluble by-products in the zeolite, in which the soluble by-products are Na^+ , Cl^- , Al^{3+} and Si^{4+} etc., and most of them are Na^+ , Cl^- , Al^{3+} ;
- (2) A feedstock comprising of 10~50% by weight, preferred 15~40% by weight of the rare-earth Y-zeolite obtained in step (1), 10~60% by weight, preferred 15~40% by weight of a binder, and 2~75% by weight, preferred 20~60% by weight of a clay is

mixed and pulped, and formed by spray drying.

In the method provided by present invention, the preparing process of the rare-earth Y-zeolite disclosed in step (1) has been described in the application of CN01115612.0 by the inventor. Based on the gas phase chemical method of SiCl_4 and the facile diffusibility of the substance in gaseous state, SiCl_4 with dynamics radius of 0.687nm was introduced in gaseous state into the channels of the zeolite in this preparing process. In effective combination with the high ion exchange capacity of NaY zeolite, the isomorphous replacement reaction was carried out with the dealumination and the supplement of silica.

The rare-earth Y-zeolite disclosed in step (1) may be the REY and REHY zeolite widely used in industry, and also the product of the NaY zeolite exchanged rare-earth ion.

In general, the rare-earth content of REHY zeolite, calculated in RE_2O_3 , is from 6 to 16% by weight and the Na_2O content is more than 4% by weight. The rare-earth content of REY zeolite, calculated in RE_2O_3 , is from 10 to 18% by weight and the Na_2O content is more than 2% by weight. The rare-earth ion exchange process of NaY zeolite is carried out by exchanging the NaY zeolite with Si/Al ratio higher than 3.5 and the rare-earth chloride solution in a weight ratio of $\text{NaY} : \text{RECl}_3 : \text{H}_2\text{O} = 1 : 0.1 \sim 0.25 : 5 \sim 15$ at $80 \sim 90^\circ\text{C}$ for 30 to 60min under a pH more than 3.5, and then with or without drying.

In the method of present invention, the REHY and REY raw materials or the NaY zeolite ion exchanged with the rare-earth chloride solution used to prepare the rare-earth Y-zeolite disclosed in step (1) have to be dried prior to the reaction so that their water contents are less than 10% by weight, preferred less than 5% by weight.

In the method of present invention, the binder disclosed in step (2) is selected from one or more of pseudoboehmite, alumina sol, silica sol and phosphorus-alumina sol, preferred the double-alumina binder, in which the weight ratio of pseudoboehmite and alumina sol is 10~40: 0~30, preferred 15~25: 2~25. When the double-alumina binder is used, the weight ratio of acid and alumina in the acid treatment of pseudoboehmite is 0.1~0.6: 1, preferred 0.15~0.35: 1. Generally the acid treatment is proceeded at $40 \sim 90^\circ\text{C}$ for 0.5 to 6 hours by adding hydrochloric acid. The pseudoboehmite after acid treatment can be used with alumina sol or phosphorus-alumina sol.

In the method of present invention, the clay is the clay usually used in cracking catalyst matrix, such as Kaolin, halloysite, montmorillonite, bentonite or sepiolite, etc.

In the method of present invention, the catalyst is obtained by pulping the feedstock comprising of a zeolite, a clay and a binder in conventional method, homogenizing, spray-drying with inlet temperature of 550~600°C and outlet temperature of 250~300 °C.

The catalyst provided in present invention can be used to treat all kinds of raw oil, especially the inferior raw oil, such as all kinds of residuum (heavy oil). The residuum mainly includes full atmospheric residuum, distilled oil blended with atmospheric residuum and distilled oil blended with vacuumed residuum.

The catalyst provided in present invention, comparing to the catalyst using REUSY, REHY, REY and P-REHY as cracking active component in the prior art, is characterized with good cracking activity, high hydrothermal stability, and high conversion of heavy oil as well as excellent selectivity of gasoline, dry gas and coke. The olefin content in the produced gasoline decreases effectively due to the high hydrogen transfer activity. The zeolite content of the catalyst decreases 5~25% compared to the catalyst prepared in prior art for cracking the heavy oil and decreasing the olefin content.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is the FT-IR spectra of the hydroxyl structure of the zeolite used in the catalyst after 100% steam-aging treatment at 800°C for 17 hours.

Figure 2 is a graph of B-acid for the zeolite used in the catalyst after 100% steam-aging treatment at 800°C for 17 hours.

Figure 3 is the BET graph of the catalyst after steam-aging treatment.

EMBODIMENTS

The following examples are used to illustrate the present invention.

In the examples and comparative examples the hydroxyl structural spectra and the acidity graph of the samples were characterized by FT-IR.

In the examples, the RE_2O_3 and Al_2O_3 contents of the samples were measured by fluorometry. The specific surface area and pore volume were measured by low temperature nitrogen adsorption-desorption method.

The micro activity test on light oil is proceeded at 460°C by using Dagang light diesel with a distillation range of $235\sim 335^\circ\text{C}$ as feedstock, and the catalyst-oil ratio of 3.2 and the weight hourly space velocity (WHSV) of 16h^{-1} .

The micro activity test on heavy oil is proceeded at 482°C with a catalyst-oil ratio of 4.

Examples 1~7 are used to illustrate the preparing procedure and physical-chemical parameters of the rare-earth Y-zeolite in the catalyst disclosed in present invention.

Example 1

NaY zeolite with a dry basis of 85% (a Si/Al ratio of 4.0, a unit cell size of 2.473nm , a Al_2O_3 content of 24.8%, a Na_2O content of 16%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was ion exchanged with a rare-earth solution in a ratio of $\text{NaY}:\text{RECl}_3:\text{H}_2\text{O}=1:0.21:10$ at $80\sim 90^\circ\text{C}$ for 60min, and dried till the water content was less than 10% and the RE_2O_3 content was 16%, in which La_2O_3 content was 4.16%, Ce_2O_3 content was 8.16%, and the content of other rare-earth oxides was 3.68%. In a ratio of $\text{NaY}:\text{SiCl}_4=1:0.4$, the ion exchanged NaY zeolite reacted with SiCl_4 gas carried by dry air at 550°C for 120min, and purged with dry air for 20min, and then washed and filtrated to remove Cl^- and Na^+ , and obtained a sample, designated as RHSY-1. The physical-chemical parameters are listed in table 1.

Example 2

NaY zeolite with a dry basis of 75% (a Si/Al ratio of 5.05, a unit cell size of 2.466nm , a Al_2O_3 content of 21.2%, a Na_2O content of 15.8%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was ion exchanged with a rare-earth solution in a ratio of $\text{NaY}:\text{RECl}_3:\text{H}_2\text{O}=1:0.25:10$ at $80\sim 95^\circ\text{C}$ for 40min, and then was filtrated, washed, dried and dehydrated. In a ratio of $\text{NaY}:\text{SiCl}_4=1:0.25$, the ion exchanged NaY zeolite reacted with SiCl_4 gas carried by dry air at 450°C for 60min and purged

with dry air for 120min, and then washed and filtrated to obtain a sample, designated as RHSY-2. The physical-chemical parameters are listed in table 1.

Example 3

REHY zeolite (a RE_2O_3 content of 13.4%, in which a La_2O_3 content of 10.7%, a Ce_2O_3 content of 2.1%, a content of other rare-earth oxides of 0.6%, a unit cell size of 2.469nm, a differential thermal collapse temperature of 985°C, a Na_2O content of 4.4%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was put into a reactor to be dried till the water content less than 5%. Then in a ratio of REHY: $SiCl_4$ = 1: 0.75, the dried REHY zeolite reacted with $SiCl_4$ gas carried by dry air at 350°C for 3 hours and purged with dry air for 60min. and then washed and filtrated to obtain a sample, designated as RHSY-3. The physical-chemical parameters are listed in table 1.

Example 4

NaY zeolite with a dry basis of 85% (a Si/Al ratio of 4.0, a unit cell size of 2.473nm, a Al_2O_3 content of 24.8%, a Na_2O content of 16%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was ion exchanged with a rare-earth solution in a ratio of NaY: $RECl_3$: H_2O =1: 0.21: 10 at 80~90°C for 60min, and dried till the water content was less than 7% and the RE_2O_3 content was 16%, in which La_2O_3 content was 4.16%, Ce_2O_3 content was 8.16%, and the content of other rare-earth oxides was 3.68%. In a ratio of NaY: $SiCl_4$ =1: 0.5, the ion exchanged NaY zeolite reacted with $SiCl_4$ gas carried by dry air at 300°C for 5 hours, and purged with dry air for 20min, and then washed and filtrated to obtain a sample, designated as RHSY-4. The physical-chemical parameters are listed in table 1. The spectra of the hydroxyl structure and the acidity graph of RHSY-4 characterized by FT-IR after 100% steam-aging treatment at 800°C for 17 hours are shown in Figures 1 and 2 respectively.

Example 5

REY zeolite with a dry basis of 85% (a RE_2O_3 content of 18.8%, in which a La_2O_3 content of 14.8%, a Ce_2O_3 content of 2.9%, a content of other rare-earth oxides of 1.1%,

a unit cell size of 2.469nm, a differential thermal collapse temperature of 980°C, a Na₂O content of 2.7%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was put into a reactor to be dried till the water content less than 5%. Then in a ratio of REHY: SiCl₄ = 1: 0.8, the dried REY zeolite reacted with SiCl₄ gas carried by dry air at 350°C for 120min and purged with dry air for 20min, and then washed and filtrated to obtain a sample, designated as RHSY-5. The physical-chemical parameters are listed in table 1.

Example 6

NaY zeolite with a dry basis of 85% (a Si/Al ratio of 4.0, a unit cell size of 2.473nm, a Al₂O₃ content of 24.8%, a Na₂O content of 16%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was ion exchanged with a rare-earth solution in a ratio of NaY: RECl₃: H₂O=1: 0.25: 10 at 80~90°C for 60min, and the RE₂O₃ content was 16%, in which La₂O₃ content was 4.16%, Ce₂O₃ content was 8.16%, and the content of other rare-earth oxides was 3.68%. In a ratio of NaY: SiCl₄=1: 0.4, the ion exchanged NaY zeolite reacted with SiCl₄ gas carried by dry air at 300°C for 4 hours, and purged with dry air for 20min, and then washed and filtrated to obtain a sample, designated as RHSY-6. The physical-chemical parameters are listed in table 1.

Example 7

NaY zeolite with a dry basis of 75% (a Si/Al ratio of 5.05, a unit cell size of 2.466nm, a Al₂O₃ content of 21.2%, a Na₂O content of 15.8%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) was ion exchanged with a rare-earth solution in a ratio of NaY: RECl₃: H₂O=1: 0.20: 10 at 80~95°C for 40min, then filtrated and washed. In a ratio of NaY: SiCl₄ = 1: 0.3, the ion exchanged NaY zeolite reacted with SiCl₄ gas carried by dry air at 250°C for 60min and purged with dry air for 120min, and then washed and filtrated to obtain a sample, designated as RHSY-7. The physical-chemical parameters are listed in table 1.

Comparative Example 1

Using REY zeolite (a RE_2O_3 content of 16.6%, in which a La_2O_3 content of 12.9%, a Ce_2O_3 content of 2.1%, a content of other rare-earth oxides of 1.1%, a unit cell size of 2.470nm, a differential thermal collapse temperature of 980°C, a Na_2O content of 2.7%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) as comparative sample, its physical-chemical parameters are listed in table 1. The spectra of the hydroxyl structure and the acidity graph of the REY zeolite characterized by FT-IR after 100% steam-aging treatment at 800°C for 17 hours are shown in Figures 1 and 2 respectively.

Comparative Example 2

Using REHY zeolite (a RE_2O_3 content of 13.6%, in which a La_2O_3 content of 11.4%, a Ce_2O_3 content of 1.9%, a content of other rare-earth oxides of 0.3%, a unit cell size of 2.469nm, a differential thermal collapse temperature of 985°C, a Na_2O content of 4.4%, produced by Zhoucun Catalyst Factory, Qilu Petrochemical Company) as comparative sample, its physical-chemical parameters are listed in table 1. The spectra of the hydroxyl structure and the acidity graph of the REY zeolite characterized by FT-IR after 100% steam-aging treatment at 800°C for 17 hours are shown in Figures 1 and 2 respectively.

Table 1

Example	Zeolite code	Original unit cell size (nm)	RE ₂ O ₃ (w%)	Na ₂ O (w%)	DTA (°C)	Equilibrium unit cell size (nm)
1	RHSY-1	2.440	4	0.48	1010	2.435
2	RHSY-2	2.455	7	0.43	1020	2.438
3	RHSY-3	2.457	8.9	0.35	1016	2.442
4	RHSY-4	2.460	10	0.49	1018	2.445
5	RHSY-5	2.465	15.0	0.43	1020	2.451
6	RHSY-6	2.459	13.2	0.32	1010	2.448
7	RHSY-7	2.450	11.8	0.30	1001	2.445
Comparative example 1	REY	2.470	16.6	2.7	980	2.430
Comparative example 2	REHY	2.469	13.6	4.4	985	2.426

The following examples are used to illustrate the preparing procedure of the catalyst disclosed in present invention.

Example 8

2.0 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 10.7 kg decationized water and stirred for 1.5 hours. 0.8 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. 0.036L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 2 kg alumina sol (an Al₂O₃ content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 1 hour. Finally 1.8 kg rare-earth Y-zeolite RHSY-1 (80% dry basis) prepared in Example 1 was added and stirred for 0.5 hour. The catalyst was obtained by spray drying and designated as RC-1. The properties of the catalyst are shown in Table 2.

Comparative Example 3

This comparative example is used to illustrate the preparing procedure of the catalyst

using REUSY as Y-zeolite.

2.1 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 10.7 kg decationized water and stirred for 1.5 hours. 0.65 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. 0.036L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 2 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred homogenously. The mixed rare-earth chloride solution (concentration of RE_2O_3 285g/l) was added, and ammonia was used to adjust pH to about 3 and stirred for 0.5 hour. Finally 2.3 kg REUSY zeolite (a unit cell size of 2.450nm, a RE_2O_3 content of 3%, a Na_2O content of 1.0%, 78% dry basis, produced by Qilu Catalyst Factory) was added and stirred for 0.5 hour. The catalyst was obtained by spray drying and designated as DM-1. The properties of the catalyst are shown in Table 3.

Example 9

1.9 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 20 kg decationized water and stirred for 1.5 hours. 1.5 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. 0.036L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 1.9 kg rare-earth Y-zeolite RHSY-2 (75% dry basis) prepared in Example 2 was added and stirred for 0.5 hour. The catalyst was obtained by spray drying and designated as RC-2. The properties of the catalyst are shown in Table 2.

Comparative Example 4

This comparative example is used to illustrate the preparing procedure of the catalyst using REHY and REUSY as Y-zeolite.

9.3 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 16 kg decationized water and stirred for 1 hour. 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for

another 1 hour. 0.16L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 1.9 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 0.5 hour. Then 5.1 kg REHY zeolite (a unit cell size of 2.469nm, a RE_2O_3 content of 8.8%, a Na_2O content of 4.2%, 85% dry basis, produced by Qilu Catalyst Factory) prepared by hydrothermal method and ion exchange process, and 2.7 kg REUSY zeolite (a unit cell size of 2.450nm, a RE_2O_3 content of 3%, a Na_2O content of 1.0%, 78% dry basis, produced by Qilu Catalyst Factory) were added and stirred for 0.5 hour. The catalyst was obtained by spray drying and washing with decationized water, designated as DM-2. The properties of the catalyst are shown in Table 3.

Example 10

1.7 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 15 kg decationized water and stirred for 1 hours. Then 4 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was added and stirred for 1 hour. Finally 1.4 kg rare-earth Y-zeolite RHSY-3 (85% dry basis, a RE_2O_3 content of 8.9%, a Na_2O content of 0.48%, a differential thermal collapse temperature of 1015°C) prepared in Example 3 was added and stirred for 0.5 hour. The catalyst was obtained by spray drying and designated as RC-3. The properties of the catalyst are shown in Table 2.

Example 11

2.2 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 24 kg decationized water and stirred for 1.5 hours. 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. 0.04L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 1.9 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 0.5 hour. Then 2 kg rare-earth Y-zeolite RHSY-4 (78% dry basis) prepared in Example 4 was added and stirred for 1 hour. The catalyst was obtained by spray drying

and designated as RC-4. The properties of the catalyst are shown in Table 2.

Comparative Example 5

This comparative example is used to illustrate the preparing procedure of the comparative catalyst using P-REHY and ZRP as zeolite, using alumina sol and pseudoboehmite as binder.

1.6 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 21 kg decationized water and stirred for 1 hour. Then 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. Finally 0.04L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 1.9 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 1 hour. Then 1.8 kg phosphorus rare-earth hydrogen Y-zeolite P-REHY-1 (a unit cell size of 2.469nm, a RE_2O_3 content of 8.2%, a Na_2O content of 1.1%, a P_2O_5 content of 2.4%, 85% dry basis, produced by Qilu Catalyst Factory) and 0.09 kg ZRP zeolite (a Si/Al ratio of 50, a Na_2O content less than 1%, 90% dry basis, produced by Qilu Catalyst Factory) were added and stirred for 1 hour. The catalyst was obtained by spray drying and washing with decationized water, designated as DM-3. The properties of the catalyst are shown in Table 3.

Example 12

2.2 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 16.7 kg decationized water and stirred for 1 hour. Then 4.7 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was added and stirred for 1 hour. Finally 1.1 kg rare-earth Y-zeolite RHSV-5 (78% dry basis) prepared in Example 5 and 0.06 kg ZRP zeolite (a Si/Al ratio of 50, a Na_2O content less than 1%, 90% dry basis, produced by Qilu Catalyst Factory) were added and stirred for 1 hours. The catalyst was obtained by spray drying and designated as RC-5. The properties of the catalyst are shown in Table 2.

Comparative Example 6

This comparative example is used to illustrate the preparing procedure of the catalyst using P-REHY and ZRP as zeolite.

2.2 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 16.7 kg decationized water and stirred for 1 hour. Then 4.7 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was added and stirred for 1 hour. Finally 2.2 kg phosphorus rare-earth hydrogen Y-zeolite P-REHY-2 zeolite (a unit cell size of 2.467nm, a RE_2O_3 content of 9%, a Na_2O content of 1.1%, a P_2O_5 content of 2.0%, 85% dry basis, produced by Qilu Catalyst Factory) and 0.06 kg ZRP zeolite (a Si/Al ratio of 50, a Na_2O content less than 1%, 90% dry basis, produced by Qilu Catalyst Factory) were added and stirred for 1 hour. The catalyst was obtained by spray drying and washing with decationized water, designated as DM-4. The properties of the catalyst are shown in Table 3.

Example 13

2 kg Suzhou Kaolin (83% dry basis, produced by Chinese Kaolin Company) was added into 15 kg decationized water and stirred for 1 hour. Then 3.9 kg silica sol (a SiO_2 content of 15.5%, produced by Beijing Changhong Middle School Chemical Factory) was mixed homogenously. Finally 0.72 kg rare-earth Y-zeolite RHSY-5 (78% dry basis) prepared in Example 5 was added and stirred for 1 hour. The catalyst was obtained by spray drying and designated as RC-6. The properties of the catalyst are shown in Table 2.

Example 14

3.7 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 20 kg decationized water and stirred for 1.5 hours. Then 1.5 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. Finally 0.25L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. Then 1.5 kg rare-earth Y-zeolite RHSY-6 (78% dry basis) prepared in Example 6 was added and

stirred for 1 hour. The catalyst was obtained by spray drying and designated as RC-7. The properties of the catalyst are shown in Table 2.

Example 15

2.2 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 12 kg decationized water and stirred for 1.5 hours. Then 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. Finally 0.19L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. Then 0.58 kg rare-earth Y-zeolite RHSY-7 (78% dry basis) prepared in Example 7 was added and stirred for 1 hour. The catalyst was obtained by spray drying and designated as RC-8. The properties of the catalyst are shown in Table 2.

Comparative Example 8

This comparative example is used to illustrate the preparing procedure of the catalyst using REHY as zeolite.

2.3 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 20 kg decationized water and stirred for 1 hour. Then 1 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. Finally 0.2L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 2.3 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 0.5 hour. Then 2.1 kg REHY zeolite (a unit cell size of 2.469nm, a RE_2O_3 content of 8.2%, a Na_2O content of 4.2%, 83% dry basis, produced by Qilu Catalyst Factory) was added and stirred for 1 hour. The catalyst was obtained by spray drying and washing with decationized water, designated as DM-5. The properties of the catalyst are shown in Table 3.

Comparative Example 9

This comparative example is used to illustrate the preparing procedure of the

comparative catalyst using REY as zeolite.

1.6 kg Suzhou Kaolin (85% dry basis, produced by Chinese Kaolin Company) was added into 16 kg decationized water and stirred for 1 hour. Then 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Alumina Company) was added and stirred for another 1 hour. Finally 0.16L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 1.9 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 0.5 hour. Then 2.1 kg rare-earth zeolite REY (a unit cell size of 2.467nm, a RE_2O_3 content of 13.7%, a Na_2O content of 4.2%, 90% dry basis, produced by Qilu Catalyst Factory) was added and stirred for 1 hour. The catalyst was obtained by spray drying and washing with decationized water, designated as DM-6. The properties of the catalyst are shown in Table 3.

Example 16

1.6 kg Suzhou Kaolin (73% dry basis, produced by Chinese Kaolin Company) was added into 15 kg decationized water and stirred for 1 hour. Then 1.2 kg pseudoboehmite (65% dry basis, produced by Shandong Aluminium Company) was added and stirred for another 1 hour. Finally 0.19L HCl (industry grade) was added and stirred for 10min. The obtained slurry was heated to 60°C and aged for 1 hour. 0.7 kg alumina sol (an Al_2O_3 content of 21.5%, produced by Qilu Catalyst Factory) was mixed with the slurry and stirred for 0.5 hour. Then 1.27 kg rare-earth Y-zeolite RHSY-3 (85% dry basis) prepared in Example 3 was added and stirred for 1 hour. The catalyst was obtained by spray drying and designated as RC-9. The properties of the catalyst are shown in Table 2.

Table 2

Example	Catalyst	Al ₂ O ₃ (w%)	RE ₂ O ₃ (w%)	Na ₂ O (w%)	Specific surface area (m ² /g)	nitrogen adsorption		abrasive index
						V _{Pore}	V _{micro}	
8	RC-1	42.9	1.4	0.17	266	0.184	0.094	0.2
9	RC-2	47.9	2.4	0.12	268	0.192	0.087	1.2
10	RC-3	40.9	3.1	0.16	290	0.181	0.110	0.2
11	RC-4	55	3.5	0.14	212	0.171	0.55	1.4
12	RC-5	49	3.6	0.17	254	0.190	0.080	1.6
13	RC-6	48	3.0	0.09	260	0.184	0.094	1.4
14	RC-7	50	3.2	0.06	270	0.190	0.090	1.2
15	RC-8	48	1.8	0.12	265	0.194	0.98	1.7
16	RC-9	46.6	3.0	0.18	303	0.203	0.089	2.0

Table 3

Comparative example	Catalyst	Al ₂ O ₃ (w%)	RE ₂ O ₃ (w%)	Na ₂ O (w%)	Specific surface area (m ² /g)	nitrogen adsorption		Abra- sive index
						V _{Pore}	V _{micro}	
1	DM-1	49.5	1.7	0.35	268	0.178	0.083	2.3
2	DM-2	55	2.5	0.38	263	0.210	0.086	2.4
3	DM-3	51	3.2	0.38	272	0.188	0.073	2.3
4	DM-4	50	3.6	0.32	262	0.199	0.073	1.7
5	DM-5	57	3.2	0.22	260	0.199	0.073	1.8
6	DM-6	57	5.5	0.16	242	0.181	0.067	1.9

The following examples are used to illustrate the cracking properties of the catalyst disclosed in present invention for all kinds of hydrocarbon raw oils.

Example 17

The catalytic cracking of raw oil I (Liaohe wax oil, its properties shown in Table 4) was carried out in a fixed fluid-bed unit at 500°C with a weight hourly space velocity (WHSV) of 12h⁻¹, a catalyst-oil ratio of 5, and a water content(based on raw material) of 10% by weight, by using catalysts RC-1, RC-3 (with a rare-earth Y-zeolite content of 35% by weight) and the comparative catalyst DM-1 (with a zeolite content of 40% by weight) disclosed in present invention as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 8 hours under a 100% steam atmosphere. The reaction results are listed in Table 5.

Table 4

Raw oil I	
Density, g/cm ³ (20°C)	0.9275
Viscosity, mm ² /(50°C)	52.15
(80°C)	14.93
Freeze point, °C	28
Carbon residue, w%	0.25
Basic nitrogen, ppm	795
Element analysis, w%	
C	86.6
H	12.04
S	0.32
N	1
PNOA analysis, w%	
Paraffin	67.5
Aromatic	23
Colloid	9.5
Bitumen	0
Vacuum distillation range, °C	
IBP	265
5%	320
10%	343
30%	398
50%	429
70%	455
90%	504

Table 5

Catalyst code		RC-3	RC-1	DM-1
Product distribution w%	Dry gas	2.12	2.01	19.0
	LPG	14.23	13.04	14.05
	GLN	52.38	49.33	47.15
	LCO	17.36	19.57	19.93
	Heavy oil	9.57	13.01	13.57
	Coke	4.24	3.04	3.40
	Conversion	73.07	67.42	66.50
	Light oil yield	69.74	68.90	67.08
	LPG+GLN+LCO	84.07	81.94	81.13

As seen from Table 5, the catalysts RC-1 and RC-3 provided in present invention have high conversion for heavy oil. The un-converted content of heavy oil is less than that of comparative catalyst DM-1, especially for RC-3 whose un-converted content of heavy oil is lower than that of comparative catalyst DM-1 by 4%. The yield of light oil is higher than that of comparative catalyst by about 1–2%. From the view of the product distribution, the catalytic selectivity for gasoline, coke and dry gas is better than that of the comparative catalyst at almost the same conversion. So the catalyst disclosed in present invention is an excellent cracking catalyst for heavy oil.

Example 18

The catalytic cracking of raw oil II (Wuhan three-blended-residuum, its properties shown in Table 6) was carried out in a fixed fluid-bed unit at 500°C with a catalyst-oil ratio of 5 by using catalysts RC-1, RC-3 and the comparative catalyst DM-1 as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 4 hours under a 100% steam atmosphere. The obtained crude gasoline was analysed by chromatographic PNOA and the results are listed in Table 7.

Table 6

Raw Oil II	
Density, g/cm ³ (20°C)	0.9070
Viscosity, mm ² /(80°C)	17.17
Aniline point, °C	95.8
Pour point, °C	43
Refractive index, 20°C	1.5217
Conradson Carbon, w%	3.1
Basic nitrogen, ppm	1010
Element analysis, w%	
C	86.37
H	12.53
S	0.80
N	0.29
Ni, ppm	7.0
V, ppm	0.8
Distillation rang, °C	
IBP	241
10%	347
30%	413
50%	450
70%	493
80%	535
90%	-

Table 7

Catalyst	n-Paraffin NP	i-Paraffin ZP	Olefin Q	Naphthene N	Aromatic A	Octane number RON
DM-1	5.55	39.41	33.34	8.26	13.34	90.1
RC-1	4.79	51.59	17.3	8.26	18.06	91.4
RC-3	5.51	55.14	12.97	6.26	20.12	90

As seen from Table 7, the catalysts RC-1 and RC-3 provided in present invention have an obvious effect on the decrease of the olefin content of gasoline. Their olefin contents of gasoline can reach 17.3% and 12.97% respectively, lower than the olefin content 33.34% of the comparative catalyst DM-1. The contents of i-paraffin for RC-1 and RC-3 are 51.59% and 55.14%, higher than the content 39.41% of the comparative catalyst, while remaining relatively high octane numbers. So the catalyst disclosed in present invention is a desirable catalyst for decreasing the olefin content of gasoline.

Example 19

The catalytic cracking of raw oil III (Liaohe Anshan wax oil, its properties shown in Table 8) was carried out in a fixed fluid-bed unit at 510°C with a weight hourly space velocity (WHSV) of 20h⁻¹ and a catalyst-oil ratio of 5 by using the catalyst RC-2 and the comparative catalyst DM-2 disclosed in present invention as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 4 hours under a 100% steam atmosphere. The reaction results are listed in Table 9.

Table 8

Raw oil III	
Density, g/cm ³ (20°C)	0.9268
Viscosity, mm ² /(100°C)	9.072
Freeze point, °C	+31
Aniline point, °C	78.5
Carbon residue, w%	0.27
Paraffin, w%	62.0
Aromatic, w%	26.6
Colloid, w%	11.3
Bitumen, w%	0.1
Distillation rang type	D1160
Element analysis, w%	
C	87.03
H	12.15
S	0.26
N	0.28
Basic nitrogen, ppm	865
IBP	264
5%	320
10%	350
30%	411
50%	444
70%	468
90%	515

Table 9

Catalyst code		RC-2	DM-2
Analysis item			
Product distribution w%	Dry gas	2.0	2.0
	LPG	12.8	14.8
	C ₃ +C ₄	8.0	9.2
	GLN	50.5	47.2
	LCO	21.5	22.0
	Heavy oil	7.8	9.1
	Coke	4.9	4.5
	Conversion	70.2	68.5
	RON	89.0	89.4
	n-Paraffin	4.23	4.39
	i-Paraffin	43.23	40.49
	olefin	19.05	25.04
	Naphthene	8.23	9.43
	Aromatic	25.28	20.65
	MA	82	77

As seen from Table 9, comparing to the comparative catalyst DM-2 (two zeolites, with a zeolite content of 41% by weight), the catalyst RC-2 (with a zeolite content of 32% by weight) provided in present invention has high conversion for heavy oil. The yield of light oil is higher than that of the comparative catalyst by almost 2.8%. At almost the same octane number, the olefin content is decreased 6%, showing high activity for the decrease of the olefin content.

Example 20

The catalytic cracking of raw oil IV with inferior quality (Liaohe wax oil: Liaohe coking gas oil: Daqing vacuumed residuum= 55: 20: 25, its properties shown in Table 10) was carried out in a fixed fluid-bed unit at 500°C with a weight hourly space

velocity (WHSV) of 10h^{-1} and a catalyst-oil ratio of 6 by using the catalysts RC-2, RC-9 and the comparative catalyst DM-2 disclosed in present invention as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 12 hours under a 100% steam atmosphere. The reaction results are listed in Table 11.

The crude gasoline obtained by using catalyst RC-9 and comparative catalyst DM-2 in a fixed fluid-bed unit was analysed by PNOA analysis and the results are listed in Table 12.

Table 10

Raw oil IV	
Density, g/cm ³ (20°C)	0.9213
Carbon residue, w%	23
Freeze point, °C	33.0
Viscosity, mm ² /(80°C)	14.00
Refractive index, (70°C)	1.4974
Aniline point, °C	97.2
Element analysis, w%	
C	86.86
H	12.29
S	0.24
N	0.31
PNOA analysis, w%	
Paraffin	56.0
Aromatic	27.8
Colloid	16.2
Bitumen	0.0
Metal content, m%	
Fe	5.0
Ni	3.6
Cu	<0.1
V	<0.1
Ca	2.5
Distillation, °C	
IBP	212
5%	329
10%	363
30%	422
50%	458
70%	518

Table 11

Catalyst code	RC-2	RC-9	DM-2
WHSV, h ⁻¹	10.0	9.8	9.8
H ₂ -C ₂	2.01	2.01	1.69
C ₃ -C ₄	14.64	13.91	15.33
GLN(C ₅ -221°C)	54.94	57.80	52.86
LCO(221-300°C)	12.92	11.52	12.97
Heavy oil (heavy oil °C)	8.15	7.04	9.73
Coke	7.34	7.72	7.42
Conversion, w%	78.93	81.44	77.30
Light oil yield, w%	67.86	69.32	65.83
Product selectivity			
H ₂ -C ₂ , Conversion	0.026	0.025	0.022
C ₃ +C ₄ , Conversion	0.185	0.171	0.198
GLN, Conversion	0.696	0.710	0.684
Coke, Conversion	0.093	0.095	0.096
Octane number (GC)			
MON	78.7	78.1	78.6
RON	89.4	88.6	89.1

As seen from Table 11, the catalysts RC-2 and RC-9 (with a zeolite content of 32% and 35% by weight respectively) provided in present invention have much higher cracking activity for heavy oil than that of the comparative catalyst DM-2 (with a zeolite content of 41% by weight) under the conditions of lower zeolite content and same supporter. The yield of light oil is higher than that of the comparative catalyst by almost 2~3.5%. Both the selectivity of gasoline and the selectivity of coke are better than that of the comparative catalyst.

Table 12

Catalyst	PNOA analysis, w%			
	Paraffin	Olefin	Naphthene	Aromatic
DM-2	38.49	26.12	10.30	25.09
RC-9	42.55	22.59	9.65	25.21

As seen from Table 12, the catalyst provided in present invention still shows the activity for decrease of the olefin content even used in the cracking of the inferior raw oil.

Example 21

The catalytic cracking of raw oil V (Daqing atmospheric residuum: Aman = 20: 80) was carried out in a fixed fluid-bed unit at 520°C with a weight hourly space velocity (WHSV) of 30h⁻¹ and a catalyst-oil ratio of 4 by using the catalyst RC-4 and the comparative catalysts DM-5 and DM-6 disclosed in present invention as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 4 hours under a 100% steam atmosphere. The reaction results are listed in Table 13.

Table 13

Catalyst code		RC-4	DM-5	DM-6
Analysis item				
Zeolite	Type	RHSY	REHY	REY
	Content, %	35	35	35
	RE ₂ O ₃ , w%	3.5	2.8	5.5
Product distribution w%	Dry gas	1.6	2.0	1.9
	LPG	12.0	12.4	11.7
	GLN	49.2	48.2	49.0
	LCO	21.4	20.8	21.1
	Heavy oil	9.6	9.5	9.0
	Coke	5.7	6.6	6.7
	Conversion	68.5	69.2	69.3
	GLN+LCO	70.6	69	70.1
	GLN+LCO+LPG	82.6	81.4	81.8
	RON	88.3	89.5	89.9
	Olefin	25.82	27.65	23.69

As seen from Table 13, comparing to the comparative catalysts DM-5 with REHY zeolite and DM-6 with REY zeolite, the catalyst provided in present invention has high yield of light oil at the similar conversion and the activity to decrease the olefin content as well as the excellent selectivity of the coke.

Example 22

The catalytic cracking of raw oil VI (Daqing atmospheric residuum, its properties shown in Table 14) was carried out in a fixed fluid-bed unit at 500°C with a weight hourly space velocity (WHSV) of 30h⁻¹ and a catalyst-oil ratio of 4 by using the catalyst RC-4 and the comparative catalysts DM-3 (catalyst special for decreasing the olefin content) disclosed in present invention as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 8 hours under a 100% steam atmosphere. The reaction

results are listed in Table 15.

Table 14

Raw oil VI	
Density, g/cm ³ (20°C)	0.8906
Viscosity, mm ² /(80°C)	44.18
mm ² / (80°C)	24.84
Freeze point, °C	43
Aniline point, °C	>105
Conradson carbon, w%	4.3
C/O ₂ , mol/mol	0.55
Bromine value, gBr/100g	3.6
Refractive index, n _D ²⁰	1.4957
Element analysis, w%	
C	86.54
H	13.03
S	0.3
N	0.13
PNOA analysis, w%	
Paraffin	51.2
Aromatic	29.7
Colloid	18.3
Bitumen	0.8
Distillation range, °C	
IBP	
5%	282
10%	351
30%	370
50%	482
70%	353

Table 15

Analysis item	Catalyst code	
	RC-4	DM-4
RE ₂ O ₃ , w%	3.2	3.6
LPG	11.2	15.5
GLN	51.9	50.1
LCO	19.5	19.1
Heavy oil	8.9	7.3
Coke	7.6	7.5
Conversion	71.1	73.1
GLN+LCO	71.4	69.2
RON	86.3	89.0
n-Paraffin	5.30	4.28
i-Paraffin	45.61	43.05
Olefin	28.33	33.95
Naphthene	10.64	9.70
Aromatic	10.12	9.03
MA	69	73

As seen from Table 15, even the catalyst RC-4 disclosed in present invention has lower zeolite content than the comparative catalyst DM-4 by 5% and has no ZRP zeolite, it has high conversion for heavy oil. The yield of light oil is higher than that of the comparative catalyst by almost 2% and the olefin content is lower than that of the comparative catalyst by 5%. The catalyst possesses the activity to decrease the olefin content.

Example 23

The micro activity test on heavy oil was carried out by using the catalysts RC-5, RC-6, RC-7 and the comparative catalyst DM-3 as catalysts. Prior to the test each catalyst to be tested was treated at 800°C for 17 hours under a 100% steam atmosphere. The reaction results are listed in Table 16.

Table 16

Catalyst code Analysis item		RC-5	RC-6	RC-7	DM-3
Zeolite content (relative)		0.60	0.75	0.60	base*
Product distribution w%	Gas	19.8	19.5	19.0	23.4
	GLN	53.0	53.2	54.8	47.5
	LCO	17.4	16.9	16.6	17.1
	Coke	1.6	1.6	1.7	1.5
	Heavy oil	8.2	8.8	7.9	10.5
	Conversion	74.4	74.3	75.5	72.4
Light oil yield		70.4	70.1	71.4	64.6
$C_4^0/C_4^=$		1.19	1.05	1.0	0.81

*: The base is 40%.

As seen from Table 16, the catalyst disclosed in present invention still has high conversion for heavy oil even with much lower zeolite content than the comparative catalyst. The yield of light oil is higher than that of the comparative catalyst by 5.5~6.8%. Particularly each activity index for hydrogen transfer activity index $\Sigma C_4^0/\Sigma C_4^=$ is higher than that of the comparative catalyst. All these indicate that the activity to decrease the olefin content of the catalyst disclosed in present invention is better than that of the conventional catalyst used to decrease the olefin content.

Example 24

The catalysts RC-1, RC-9 and the comparative catalyst DM-4 disclosed in present invention were aged at 800°C under a 100% steam atmosphere for 4 hours, 8 hours and 17 hours respectively, and then subjected to a nitrogen adsorption-desorption (BET) test.

The specific surface areas measured are shown in Figure 3.

As seen from Figure 3, the catalyst disclosed in present invention maintains high specific surface area after steam-aging treatment, indicating that the catalyst disclosed in present invention has high hydrothermal stability.

Example 25

The catalysts RC-1, RC-2, RC-3, RC-4 and comparative catalysts DM-2, DM-5, DM-6 disclosed in present invention were aged at 800°C for 17 hours under a 100% steam atmosphere respectively, and then measured for the equilibrium unit cell size of the zeolite in the catalyst by XRD . The measurement results are shown in Table 17.

Table 17

Catalyst code		Light oil micro activity, MAT	Equilibrium unit cell size, nm
Example	RC-1	62	2.437
	RC-2	64	2.438
	RC-3	65	2.444
	RC-4	66	2.446
	RC-5	63	2.448
	RC-6	69	2.453
	RC-7	66	2.449
	RC-8	68	2.446
	RC-9	64	2.445
Comparative example	DM-2	53	2.425
	DM-3	49	2.427
	DM-4	50	2.425
	DM-5	57	2.427
	DM-6	59	2.430

As seen from Table 17, the unit cell size of each catalyst disclosed in present invention is larger than 2.435nm, but the unit cell size of each comparative catalyst is smaller than 2.432nm, indicating that the catalyst disclosed in present invention has high hydrothermal stability and structural stability.